

5.2. SPECIAL PROJECTS

5.2.1. AIRCRAFT PROJECT: STRATOSPHERIC PHOTOCHEMISTRY, AEROSOLS, AND DYNAMICS EXPEDITION (SPADE)

Compact correlations between long-lived tracer molecules (e.g., CFCs, N_2O , CH_4 , and H_2O) in the stratosphere are used to calculate the average age of air samples [Pollock *et al.*, 1992], the chlorine budget of the atmosphere [Kawa *et al.*, 1992; Woodbridge *et al.*, 1995], the ozone depletion potentials of substitute CFCs [Pollock *et al.*, 1992], and lifetimes of long-lived trace gases [Plumb and Ko, 1992]. The results of tracer correlations of CFC-11, CFC-113, CH_4 , and N_2O in the midlatitudes during SPADE in November 1992 and through April and May 1993, are compared to an earlier mission, the Airborne Arctic Stratospheric Expedition (AASE-II), from August 1991 through March 1992. Trace gases whose local lifetime are longer than quasi-horizontal transport time are in climatological slope equilibrium. A scatter plot of the mixing ratio of one versus the other collapses to a compact curve because they share surfaces of constant mixing ratio [Plumb and Ko, 1992]. In general, the long-lived tracers such as N_2O , CH_4 , CFC-11, and CFC-113 reach slope equilibrium throughout the stratosphere, hence define a compact correlation when plotted against each other.

Exceptions to this general rule can occur when mixing across exchange surfaces is faster than diffusion along mixing ratio isopleths. One such exception occurred in Stratospheric Photochemistry Dynamics and Aerosols Expedition (SPADE) during the flight of May 7, 1993. Using the tracer correlations during slope equilibrium allows the calculation of lifetimes of the tracers in the stratosphere, and in some cases in the absence of tropospheric sinks, the total atmospheric lifetime of the specie.

For the first time, CH_4 measurements from an in situ GC are compared against an in situ tunable diode laser (TDL) spectrometer and three different water vapor techniques conducted during SPADE.

Experimental Methods

The Airborne Chromatograph for Atmospheric Trace Species (ACATS), was a cooperative development between CMDL and the NOAA Aeronomy Laboratory (AL). The first ACATS instrument was a single-channel GC capable of measuring CFC-11 and CFC-113 once every 120 seconds aboard the NASA ER-2 aircraft during AASE-II. The instrument remained unchanged in the November 1992 deployment of SPADE. A second GC channel was added for CH_4 measurements during the second deployment of SPADE in April and May 1993. Because of longer times required for separation of CH_4 and CO from the air peak, both channels sampled every 180 seconds. ACATS occupies a rectangular space (45.7 cm wide \times 86.4 cm long \times 20.3 cm tall) inside the AL reactive nitrogen package and mounted together inside the equipment bay (Q-bay) of the ER-2 aircraft. The two instruments shared gases on a common cylinder rack, pump motor, and data acquisition system to reduce space and

weight. The GC's sample air inlet, forward facing, L-shaped, stainless steel tubing, 6.4 mm diameter was located on the lower Q-bay hatch extending 20 cm away from the fuselage in order to sample outside the aircraft (Figure 5.18).

Typical ER-2 flight speeds of 200 m s^{-1} (0.8 mach) required faster sampling rates than commercial GCs provide to gain adequate data spacial resolution. The sampling rates are made possible by a 12-port, 2-position gas sample valve from Valco Instruments, Inc. (Houston, Texas). The gas sample valve diverts or heart-cuts the large oxygen peak away from the ECD to improve the resolution of the smaller trace species. In addition to the gas sample valve, each channel contains two gas chromatographic separation columns, a pre-column and a main column, and an ECD from Shimadzu Corp. (Tokyo, Japan). Upon injection of the sample into the GC, the gas sample valve position is switched and the carrier gas sweeps the sample 5 cm^3 for CFC channel and 15 cm^3 for CH_4 channel into the pre-column and subsequently through the main analytical separation column.

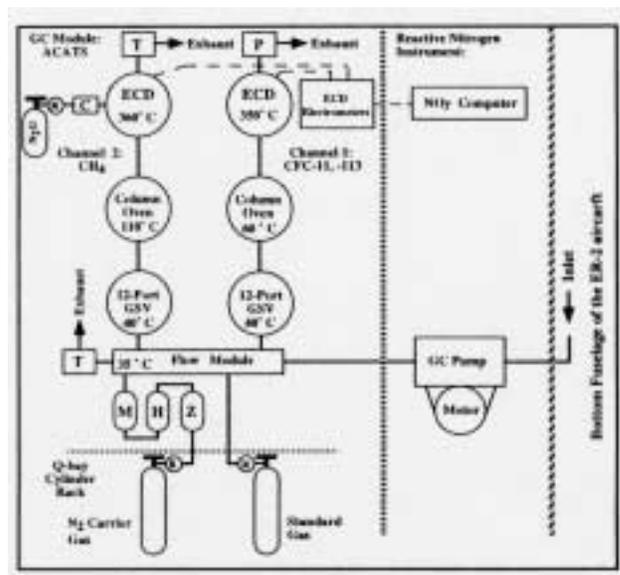


Fig. 5.18. Schematic of the ACATS. The instrument contained two separate GC channels that were used to measure CFC-11, CFC-113, and CH_4 with 180-second resolution. The nitrogen carrier gas was scrubbed in series through a hot zirconium (labeled Z) column (9.5 cc at 350°C) to remove CFCs, a Hopcalite (H) trap (manganese dioxide and copper oxide mixture, 40 cc at ambient temperature) to oxidize possible CO contamination of CO_2 , and finally a molecular sieve (M) 13X trap (40 cc at ambient temperature). The crimped (C) tubing located after the regulator (R) of the pure (N_2O) tank that delivers 20 ppm of N_2O into the ECD of channel 2. A proportional-integral-differential (PID, MKS Instruments, Massachusetts) controller (P) maintain the pressure to about $93.0 \pm 0.1 \text{ kPa}$ on the ECD of channel 1, while two pressure relief valves (T. Tavco, California) maintain separately the ECD pressure of channel 2 and the pressure of the sample loop to about $93.0 \pm 0.1 \text{ kPa}$.

Both channels share a clean supply of ultra-high purity N₂ carrier gas (99.999%, General Air, Colorado) and a stream selection array of solenoids that can supply either sample air or calibration gas while maintaining continuous flow throughout the flight.

The measurement technique for CH₄ was adapted from the work of *Goldan et al.* [1982]. The advantage of this technique is that a flame, a problem for some high-altitude applications, is not required as in the flame ionization detector for detection of CH₄. An ECD can be "sensitized" to CH₄ and CO by doping the carrier gas into the detector with mixing ratios about 15-50 ppm of nitrous oxide. Pure N₂O was delivered to the CH₄ ECD through a small piece of crimped tubing into the ECD make-up flow of ~10⁻³ cm³ min⁻¹, yielding a mixing ratio of approximately 20 ppm of N₂O in N₂ inside the ECD.

The halocarbon channel used a 1 m pre-column and a 2 m analytical column of 10% OV-101 (Analabs, Massachusetts) preconditioned at 170°C and temperature controlled at 55°C. During the course of the SPADE mission, two different column packing combinations were used on the CH₄ channel. In the first, a pre-column with a 3.2-mm o.d. and 3-m long was packed with Porapak Q (a porous polymer) was used. It was pre-conditioned at 230°C with 20-30 cm³ min⁻¹ N₂ flow for about 8 hours. The main column of 3.2-mm o.d. by 3-m was packed with molecular sieve, conditioned always to 350°C. Unfortunately, Porapak Q produced CO at temperatures above 50°C. At 100°C, mixing ratios in excess of 500 ppb of CO were found. In the second combination, a pre-column (3.2-mm o.d. by 3-m long) packed with silica gel and was preconditioned at 350°C with 20-30 cm³ min⁻¹ N₂ flow did not produce any detectable CO (>26 ppb). This pre-column was temperature controlled at 50°C with a backflush flow of 100 cm³ min⁻¹ maintained by a differential pressure flow controller (Model VCD-1000, Porter Instruments, Pennsylvania). The main column was increased to 4.8 mm o.d., with a flow controlled at 60 cm³ min⁻¹ by a mass flow controller (Model FC-260, Tylan Corp., California), and a constant temperature of 105°C. To maintain constant detector sensitivity, the ECD housing was purged with a 3 cm³ min⁻¹ flow rate of pure N₂, operated at a constant current of 1 nA, and were pressure controlled at 93 kPa. The temperatures of the ECDs on the halocarbon and CH₄/CO channels were controlled with an Omega (Stamford, Connecticut) temperature controller (Model CN9000A) at 350°C and 360°C, respectively.

Every fifth sample injection was a multi-component standard with 600 ppb of CH₄, 57 ppt of CFC-113, and 130 ppt of CFC-11. This yielded a single-point calibration every 15 minutes during a flight. Using calibrated secondary standards from the Carbon Cycle Division of CMDL in ground based checks [*Dlugokencky et al.*, 1994], showed that the calibration curve was linear for CH₄ but had a large positive intercept of ~400 ppb as a result of

interference from the oxygen peak of the sample. Thus the single-point calibration standard of 600 ppb was not sufficient to establish the calibration curve for CH₄. Values of CH₄ measured by ACATS in the troposphere were calibrated by using a correlation of CH₄ versus CFC-11 measurements [*Elkins et al.*, 1993; *Dlugokencky et al.*, 1994] from the CMDL cooperative flask station at Niwot Ridge, Colorado (40.05°N, 105.59°W, altitude 3472 m). The station resides in the midtroposphere at nearly the same latitude as Moffett Field, California (37°N, altitude 30 m). The calibration scales for CFC-11 and CFC-113 were established by comparing the instrumental response to the gravimetric standards prepared by similar techniques described in *Novelli et al.*, [1991]. The stability of the CFC-11 scale is described in *Elkins et al.*, [1993].

The other measurements used here are described in the following: from the ATLAS tunable diode laser (TDL) spectrometer [*Lowenstein et al.*, 1990, 1993] from the ALIAS TDL spectrometer [*Webster et al.*, 1994]; from the Harvard Lyman α /OH fluorescence instrument [*Hinsta et al.*, 1994]; from balloonborne frost-point hygrometers [*Oltmans*, 1985]; and H₂O from the AL Lyman α /OH fluorescence instrument [*Kelly et al.*, 1989]. The sampling of these instruments is typically 1 Hz. For use here, the data were averaged for 20 seconds before each ACATS sample, except for ATLAS N₂O that was averaged for 10 seconds. As a comparison, the AASE-II measurements CFC-11 and -113 from ACATS are included here. The AASE-II measurements and their correlation are discussed in *Woodbridge et al.*, [1995]. Measurements of CH₄ collected from flask samples using the Whole Air Sampler during AASE-II are also included [*Schauffler et al.*, 1993].

Results

During SPADE, ACATS provided measurements of CFC-11 on ten flights (November 9 and 12, 1992; April 30, May 1, 3, 6, 7, 12, 14, and 18, 1993, 1215 data points) of CFC-113 on nine flights (November 12, 1992; April 30, May 1, 3, 6, 7, 12, 14, and 18, 1993, 1117 points), and CH₄ on eight flights (April 30, May 1, 3, 6, 7, 12, 14, and 18, 1993, 970 points).

Perhaps the most interesting individual flight during the SPADE campaign was that of May 7, 1993 (see Figure 5.19). The ER-2 ascended to a cruising altitude of about 20 km (7.5 kPa) and operated in racetrack patterns such that the plane sampled the same locations several times. Three distinct levels of mixing ratios can be seen in the ACATS data. Ambient tropospheric levels of CH₄ and CFC-11 are observed during the ascent and descent. During the ascent the high CH₄ measurements (CH₄ > 1.80 ppm) were attributed to polluted air above the San Francisco Bay area. Midlatitude and polar stratospheric vortex mixing ratios were measured during the main portion of the flight. The higher mixing ratios (CH₄ ~1.40

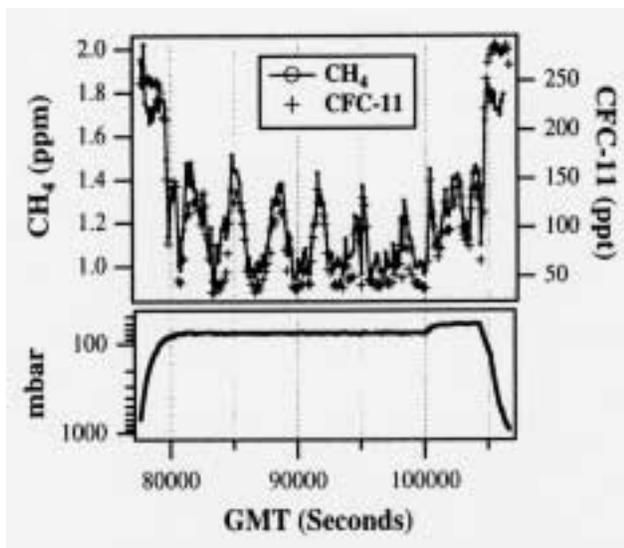


Fig. 5.19. ACATS CH_4 and CFC-11 mixing ratios measured during the flight of May 7, 1993, with accompanying pressure profile. Tropospheric measurements were observed on the ascent and descent. Two distinct air parcels with constant mixing between the air parcels were encountered in the lower stratosphere (20 km, about 7.5 kPa) as the plane repeatedly circled through the same location.

ppm and CFC-11 ~140 ppt), immediately following the ascent and throughout the constant altitude portion of the flight, are typical of midlatitude lower stratospheric air. Similar mixing ratios were measured throughout the SPADE campaign (see Figure 5.20 for complete ACATS SPADE data) and AASE-II. The low mixing ratios ($\text{CH}_4 < 1.00$ ppm and CFC-11 < 50 ppt) are levels consistent with polar vortex air measurements made during AASE-II. The polar air parcel was located near the Pacific coast (north of 37°N and west of 123.75°W) and was encountered eight separate times.

Comparison of the ACATS tracers measured during AASE-II and SPADE shows that the May 7 flight does not obey the same correlations as the remaining data, especially the CFC-11 data (Figure 5.20). This flight exhibits a breakdown in slope equilibrium where mixing between the two air parcels has not had enough time to mix along global mixing ratio isopleths. Since there is mixing between two distinctly different air parcels, a linear fit intersects the original correlation at two points, namely the initial midlatitude and polar air mixing ratios.

Figure 5.20 shows the various SPADE correlations between the long-lived tracers and the May 7 flight displayed with a plus (+) symbol. The thick, solid lines are least-square fits to the combined data sets from AASE II and SPADE: the fit spans only the range of measured mixing ratios. The two missions can be usefully combined since there was only a short time span between the missions, growth rates of the species in the stratosphere

have not changed significantly, and the missions were conducted at comparable latitudes. Drawing a linear fit through this flight (excluding the tropospheric values), the initial polar vortex CFC-11 mixing ratio can be inferred as 11 ± 5 ppt, CFC-113 as 8 ± 8 ppt, CH_4 as 870 ± 50 ppb, and N_2O as 90 ± 10 ppb. These mixing ratios are indicative of higher stratospheric air that has gone through vertical descent over the polar region, typical of values seen during AASE-II.

The correlations of CFC-11 versus N_2O and CH_4 are the most affected and may be related to the relative lifetimes of the tracers. The linear portion of the correlation plots in Figure 5.20, excluding data from May 7, can be used to calculate the stratospheric lifetime of the species, if slope equilibrium is obeyed and the ratio of the gradients of the species are nearly constant (a necessary condition for linearity) [Plumb and Ko, 1992]. Potential temperature (θ) values below 430 K were excluded to filter tropospheric values from the data. Using the arguments of Plumb and Ko [1992] for calculating steady-state lifetimes the linear relationship between two tracers can be expressed as:

$$\tau_1/\tau_2 = (\sigma_1/\sigma_2)(d\sigma_2/d\sigma_1) \quad (1)$$

where τ_1 and τ_2 are the stratospheric lifetimes as defined as the mass of the compound in the total atmosphere divided by the stratospheric loss, σ_1 and σ_2 are mixing ratios of specie 1 and 2, and $d\sigma_2/d\sigma_1$ is the slope of the linear correlation between the species. Since the growth rates of CFC-11 [Elkins et al., 1993] and CH_4 [Dlugokencky et al., 1994] have decreased to near zero, and the growth rate of N_2O is small ($0.2\text{-}0.3\%$ yr $^{-1}$), steady state can be assumed.

The fit through the CH_4 and CFC-11 correlation (containing 1013 points) is σ_{CH_4} (ppm) = $(0.0029 \pm 0.0001) \cdot \sigma_{\text{CFC-11}}$ (ppt) + (1.02 ± 0.01) , where σ_{CH_4} and $\sigma_{\text{CFC-11}}$ are the mixing ratios of each tracer. CFC-11 has no significant tropospheric sink. The stratospheric lifetime is equivalent to the atmospheric lifetime estimated to be 55 ± 8 years [Elkins et al., 1993]. The CFC-11 lifetime is the best known of all tracers measured during SPADE, because the industrial emissions are known to better than $\pm 5\%$ and because an extensive set of worldwide measurements exists for CFC-11. The calculated stratospheric CH_4 lifetime is then 129 ± 20 years and compares well with the lifetime of 147 years estimated by WMO [1991]. The large uncertainty in the calculations is proportionally divided between the uncertainty in the CFC-11 lifetime, mass of the atmosphere, the uncertainty in the mixing ratios, and a small contribution from the error in the slope.

Nitrous oxide was used as a stratospheric tracer because of its long lifetime and relatively small growth rate. The most reliable and consistent N_2O data from the AASE-II and SPADE campaigns was provided by the ATLAS

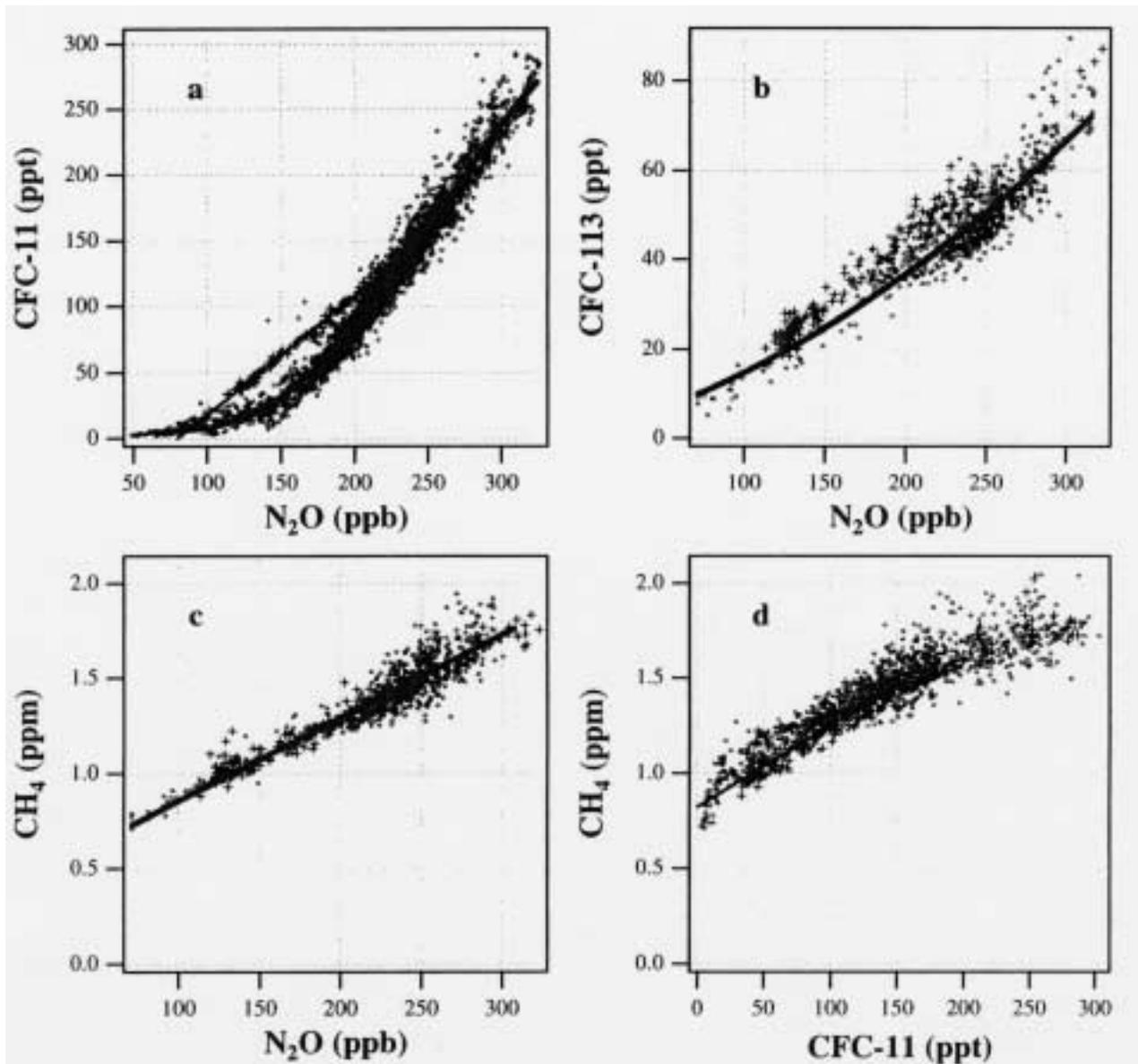


Fig. 5.20. Correlations between ACATS species for (a) CFC-11, (b) CFC-113, (c) CH₄ versus ATLAS N₂O, and (d) ACATS CH₄ versus ACATS CFC-11. The squares (■) are data for all of the ACATS SPADE flights excluding May 7, 1993, which are shown as the pluses (+). The solid lines are least squares fits through the same species by combining data from the AASE-II and SPADE missions. Both Figures 5.20a and d show considerable deviation, with respect to the flight on May 7, from the combined mission fit. This is probably the result of rapid mixing between two distinct air parcels originating from the midlatitudes and the polar regions.

instrument [Loewenstein *et al.*, 1993]. Using CFC-11 as a lifetime standard in eq. 1 and the asymptotic linear slope near the tropopause, [$\sigma_{\text{N}_2\text{O}}$ (ppb) = 0.662 ± 0.006] $\sigma_{\text{CFC-11}}$ + (143.7 ± 0.7) 2100 points] a stratospheric lifetime of 106 ± 16 years was calculated. Since there are no significant tropospheric sinks for N₂O, this value is also equal to the atmospheric lifetime. In contrast, higher estimates are reported yielding 132 years and 170 years by WMO [1991] and by Prinn *et al.*, [1990] respectively, where the latter use inverse method calculations and global tropospheric data from N₂O. Based on new absorption

cross sections for O₂ in the Schumann-Runge band, Ko *et al.*, [1991] calculate an atmospheric lifetime of 110 years using vertical profiles of N₂O from satellites and Minschwaner *et al.*, [1993] calculate a lifetime of 123 ± 20 years from balloon measurements. These results are in support of the more recent, shorter lifetime estimates.

During the SPADE campaign, both ACATS and the TDL spectrometer, ALIAS [Webster *et al.*, 1994], were measuring CH₄. A comparison between the two measurements for $\theta > 430$ K, gives a fit ALIAS σ_{CH_4} (ppm) = $(0.86 \pm 0.04) * \text{ACATS } \sigma_{\text{CH}_4} + (0.03 \pm 0.03)$ (ppm) ($r^2 =$

0.8516), where the average residual standard deviation of the fit is 0.1 ppm. This discrepancy is not within the stated experimental error limits of the ALIAS (5-10%) and ACATS (7%) instruments, and is surprising since a comparison of laboratory standards is within the errors [Webster *et al.*, 1994]. The comparison between ACATS CH₄ and CFC-11 shows tropospheric mixing ratios of the two species agree with those from the CMDL network ($\sigma_{\text{CH}_4} = 1.75$ ppm and $\sigma_{\text{CFC-11}} = 270$ ppt). The ALIAS data would give a considerably lower value of 1.52 ppm for tropospheric CH₄. Since ALIAS relies on spectroscopic parameters for calibration and not in-flight calibration, an error in either the line strength or air-broadening coefficients could be responsible for this difference. Therefore, the ACATS values were used for CH₄ for this work.

The dominant sink for stratospheric CH₄ is from oxidation by the hydroxyl radical (OH) [see Le Texier *et al.*, [1988]]. As CH₄ is oxidized, both H₂O and H₂ are produced. Molecular hydrogen is subsequently oxidized to H₂O. The rate and efficiency at which CH₄ oxidizes and the rate the remaining H₂ is oxidized leads to the production efficiency of H₂O from CH₄. In the midlatitude lower stratosphere, H₂ is produced more rapidly than H₂O and the rate at which H₂ oxidizes is slower than the CH₄ rate. Thus, the H₂ oxidation is not concurrent with CH₄ oxidation, leading to a local H₂O production expressed as dH₂O/dCH₄ of less than 2.0. Mixing with dehydrated air (occurs more often in the southern hemisphere) and mixing with low water vapor air parcels can also yield a lower production. Figure 5.21 shows three different H₂O measurements: Harvard H₂O measurements on the ER-2 aircraft, AL measurements on the ER-2 aircraft, and CMDL measurements on balloons at a nearby location, Crow's Landing, California, plotted against ACATS CH₄ conducted during SPADE. The slope

of each line gives the production that ranges from -0.8 ± 0.4 for the CMDL H₂O measurements, -1.34 ± 0.04 for AL H₂O measurements, and -1.77 ± 0.04 for the Harvard H₂O measurements. The difference between the production of H₂O cannot be the result of the CH₄ measurements since ACATS agrees well with previous CH₄ measurements of Whole Air Sampler [Schauffler *et al.*, 1993] versus AL H₂O during AASE-II (Figure 5.21). Correlation of ALIAS CH₄ with Harvard H₂O yields a slight increase in the production of H₂O (-2.28 ± 0.04) that is higher than the theoretical value at this altitude [Le Texier *et al.*, 1988]. While arguments were made by Dessler *et al.* [1994] that the production should be near 2, the absolute value of Harvard H₂O is also higher than the two other H₂O measurements.

Conclusions

Slope equilibrium is generally obeyed in the polar regions and midlatitudes at the altitudes (0-21 km) covered by the ER-2 aircraft. An exception occurs after the breakup of the polar vortex and its subsequent mixing with the midlatitudes when quasi-horizontal mixing is not fast enough to establish the original slope equilibrium. If the lifetime of one tracer is much less than the lifetime of the second tracer, a new slope on the cross-plot is established that is maintained by conservative mixing between the two air parcels. If the application of CFC-11 as a stratospheric lifetime standard is valid and slope equilibrium is obeyed, then based on the measurements presented here, the calculated lifetime of N₂O is shorter (106 ± 16 years) than previously estimated (150-170 years) by examining tropospheric N₂O budgets. Unless an unknown tropospheric sink exists, there could be large missing sources as high as 50% of the total N₂O source that remain unaccounted for in the inventory of sources.

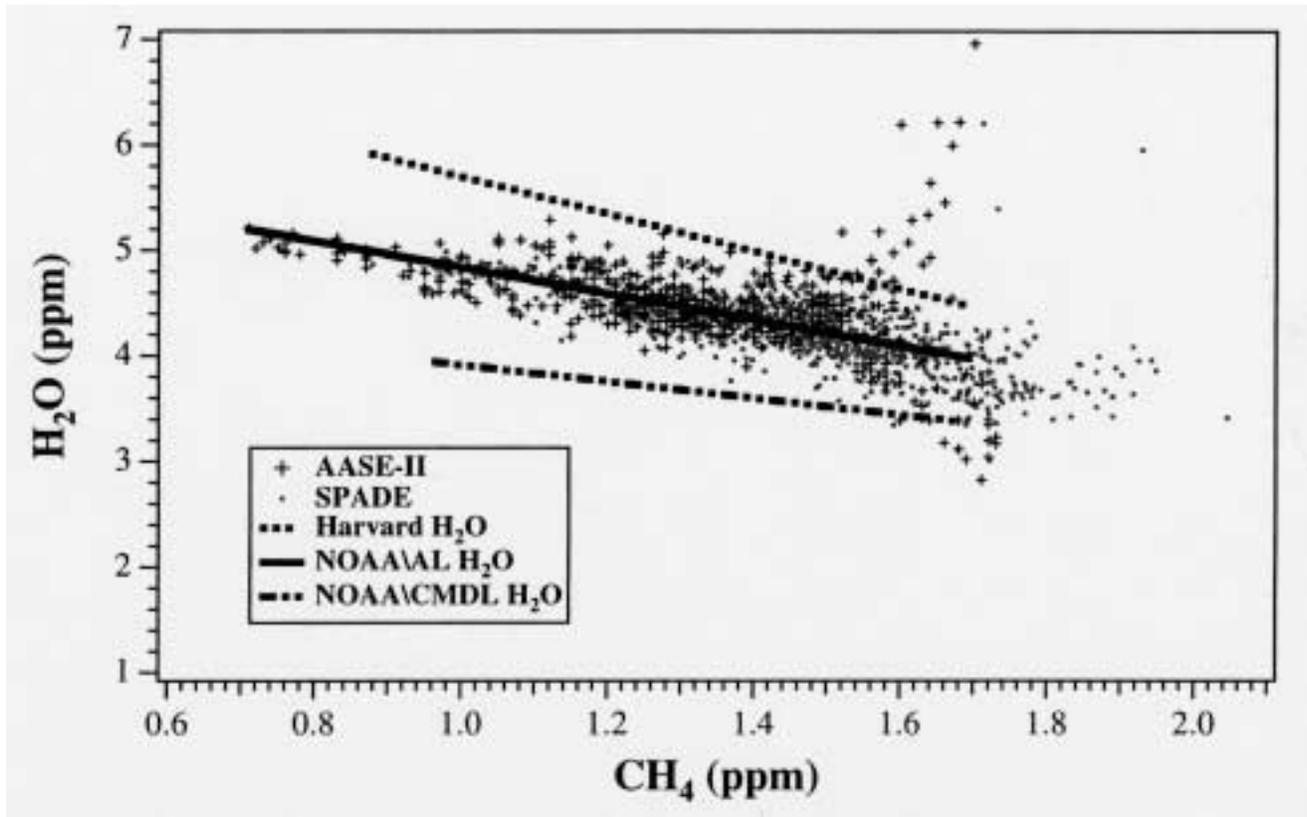


Fig. 5.21. Methane and water vapor correlations can be used to estimate the production efficiency at which CH₄ is oxidized to H₂O. The solid line is a linear fit ($y = -1.24x + 6.08$) through the combined AASE-II (+) and the SPADE (•) missions over the range CH₄ < 1.7 ppm. The absolute value of the slope is the production efficiency. The top dashed line is a similar fit ($y = -1.77x + 7.45$) using the SPADE Harvard H₂O. The bottom dashed line is $y = -0.8x + 4.7$ for ACATS CH₄ versus CMDL H₂O.